Raman spectroscopy of self-assembled InAs quantum dots in wide-bandgap matrices of AlAs and aluminium oxide

D. A. Tenne, A. G. Milekhin, A. K. Bakarov, O. R. Bajutova, V. A. Haisler, A. I. Toropov, S. Schulze,[1] and D. R. T. Zahn[1]
Institute of Semiconductor Physics, pr. Lavrenteva 13, 630090 Novosibirsk, Russia
[1]Institut für Physik, Technische Universität Chemnitz, D-09107 Chemnitz, Germany

ABSTRACT

Vibrational properties of self-assembled InAs quantum dots (QD's) embedded in AlAs and aluminium oxide were studied by Raman spectroscopy. The InAs/AlAs QD structures were grown by molecular beam epitaxy on GaAs (001) substrates. The following main features of the phonon spectra of InAs/AlAs QD nanostructures were observed: 1) asymmetric lines of QD LO phonons affected by strain, confinement and size inhomogeneity of QD's; 2) confined phonons of InAs wetting layer (WL); 3) two bands of interface phonons in the AlAs frequency region, attributed to modes associated with the planar interface WL/AlAs matrix and the three-dimensional QD/matrix interface; 4) doublets of folded acoustic phonons caused by periodicity in the multilayer QD structures. The influence of growth temperature, varied from 420 to 550°C, on the morphology of QD's was investigated. QD's grown at 420°C are found to have the smallest size. Increasing the temperature up to 480°C leads to the formation of larger InAs islands and improved size homogeneity. Further temperature elevation (above 500°C) causes partial re-evaporation of InAs leading to a decrease of QD size and density, and, finally, their complete disappearance. InAs QD's embedded in aluminium oxide were fabricated by selective oxidation of the AlAs matrix in self-assembled InAs/AlAs QD's. Micro-Raman spectroscopy data show that depending on oxidation conditions (humidity, temperature) InAs QD's in an oxide matrix can be even more strained than before oxidation, or become fully relaxed. At the boundaries of oxidized/non-oxidized areas the presence of amorphous and crystalline As clusters is evident.

INTRODUCTION

Semiconductor quantum dots (QD's) obtained by self-organized growth in highly strained heteroepitaxial systems have been intensively studied during the last decade (for a review see e.g. Refs. [1,2]). The most intensively investigated material system is InAs or InGaAs QD's in a GaAs matrix. Recently InAs QD's embedded in wide bandgap matrices of AlAs and AlGaAs have received increasing attention [3-6]. The higher barriers of the AlAs matrix produce shifts of the InAs QD bandgap energy towards the visible range as well as improved temperature stability of light-emitting devices.

Most studies of self-assembled QD's so far have been focused on their structural and electronic properties. Much less research attention has been paid to the phonon properties of QD structures. We present Raman studies of phonons in self-assembled InAs QD's in an AlAs matrix. Our results show both strain and confinement effects on the optical phonon spectra of InAs/AlAs QD's. Also we report the first Raman study of InAs QD's embedded in aluminum oxide, obtained by selective oxidation of AlAs layers in InAs/AlAs QD structures.

EXPERIMENT

We have studied a series of InAs QD's in AlAs matrix grown by molecular beam epitaxy on GaAs (001)-oriented substrates. The samples consist of five layers of InAs QD's separated by 8–12 nm AlAs spacers. In most samples studied the substrate temperature during the QD formation was 460–480°C. However, a series of InAs QD's grown at substrate temperatures varied in the range of 420–550°C was studied by Raman spectroscopy to investigate the influence of the growth temperature on the QD morphology. Special attention was given to the process of capping InAs QD's by AlAs spacer layers. To avoid an In segregation the temperature was kept the same as during the QD growth until the QD's are completely covered by AlAs. Then the growth temperature was elevated to 600°C in order to obtain a flat AlAs surface for further growth of the next QD layer.

The growth process was monitored *in situ* by reflection high-energy electron diffraction (RHEED), which showed that the transition from a two-dimensional to a three-dimensional growth mode for all the samples occurs after the deposition of 1.8 monolayers of InAs. After the deposition of the nominal amount of InAs (2 to 2.5 monolayers), the growth was interrupted for 100 s allowing self-assembled islands to reach equilibrium sizes.

High-resolution transmission electron microscopy (HRTEM) was used for structural characterization of QD structures. Figure 1 shows a typical TEM image of InAs QD's in AlAs matrix (the QD growth temperature for this sample was 460°C). According to the TEM data, QD's are vertically aligned and have the shape of truncated pyramids. HRTEM shows the InAs QD's to be pseudomorphic, i.e. the structures do not contain misfit dislocations.

Raman spectra were recorded at 80 and 300 K in a backscattering geometry in perpendicular $z(x,y)\bar{z}$ and parallel $z(x,x)\bar{z}$ polarization configurations (z axis is normal to the sample surface) using a Dilor *XY* triple spectrometer equipped with a multichannel CCD detector. Several lines of Ar^+ and Kr^+ lasers (2.41, 2.18, 1.92, 1.83, and 1.65 eV) were used for excitation.

The samples of InAs QD's embedded in Al oxide were obtained by selective wet oxidation [7] of the AlAs matrix in InAs/AlAs QD structures. After the growth of the self-assembled InAs/AlAs QD's 15 μm mesa-structures were fabricated by a standard photolithography and wet chemical etching. The mesa-structures were oxidized, and the oxidation front was investigated by micro-Raman spectroscopy (the spot size on the sample surface was ≈1 μm).

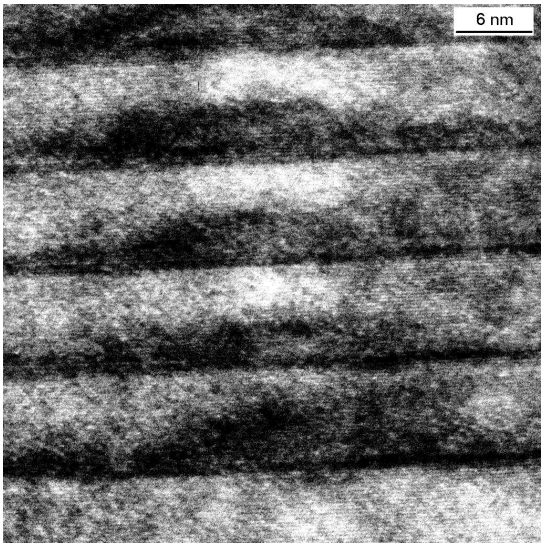

Figure 1. Cross-sectional TEM image of InAs QD's in AlAs matrix. Dark and light regions correspond to InAs QDs and AlAs layers, respectively.

RESULTS AND DISCUSSION

Figure 2 shows the characteristic Raman spectra of self-assembled InAs QD's in AlAs matrix (for a sample grown at 480°C). In the low-frequency region (Fig. 2a) the spectra contain doublet peaks of folded longitudinal acoustic phonons. The positions of the doublets agree well with the values calculated using the elastic continuum model for a superlattice with the same average period (down triangles in the Fig. 2a). Observation of the folded LA phonons in the Raman spectra of multilayer QD structures evidences their good structural quality.

Figure 2b shows the Raman spectra in the InAs optical phonon region measured with different laser lines. The shape of the InAs QD phonon lines in the Raman spectra and its dependence on the excitation energy are caused by QD size distribution and phonon confinement in small-size dots. The asymmetric phonon line shape is characteristic for Raman spectra of nanocrystalline structures. It can be described by a model of phonon confinement in nanoclusters of inhomogeneous size [8,9]. For large coherently strained InAs QD's in a GaAs matrix, where the confinement effect is negligible, the LO phonon frequency was reported to be 259-260 cm^{-1} [10-12]. This frequency is strongly shifted from the bulk InAs value (242 cm^{-1}) due to the large compressive strain. Large dots have lower energies of electronic transitions (about 1.65 – 1.7 eV for InAs QD's embedded in AlAs [5]). The contribution of these QD's to the Raman spectra is stronger for excitation lines in the red spectral range, which are closer to the resonance with electronic transitions. Therefore, at lower excitation energies the observed positions of LO phonon lines of InAs QD's (259 cm^{-1}) agree well with theoretical [10] and experimental [11,12] values for large InAs QD's in GaAs matrix. The smaller QD's have higher energies of electron and hole ground states. Therefore, the relative contribution of small dots to the Raman spectra increases at higher excitation energies. In smaller-size dots phonon confinement becomes

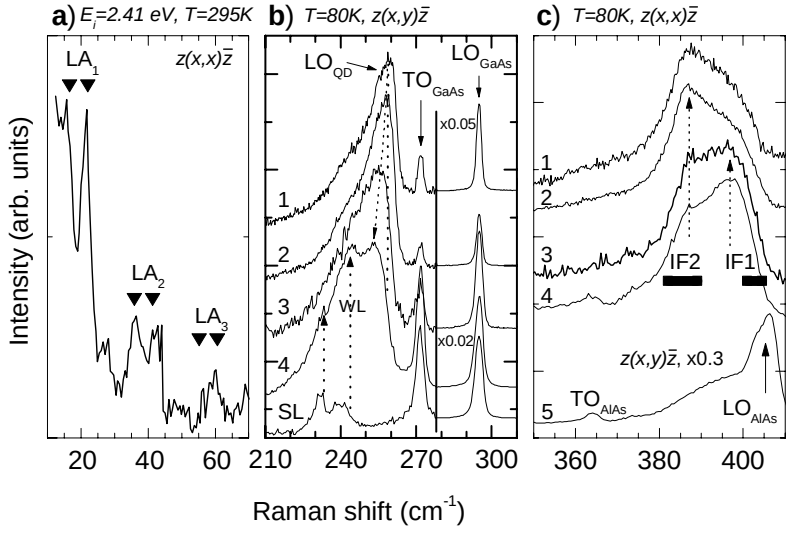

Figure 2. Typical Raman spectra of self-assembled InAs QD's in AlAs matrix (the sample shown was grown at 480°C): **a)** the low frequency region; **b)** the region of InAs and GaAs optical phonons; the spectrum marked SL is of a superlattice $(AlAs)_{30}(InAs)_{1.5}$; **c)** polarized Raman spectra in the AlAs optical phonon region; the spectrum in crossed polarization geometry, measured with 2.41 eV laser line (5) is given for comparison. In **(b)** and **(c)** the spectra 1–4 were measured with different laser lines: 1.83, 1.92, 2.18, and 2.41 eV, respectively.

more significant and causes a noticeable decrease of the phonon frequencies. For the excitation energy of 2.41 eV and the InAs/AlAs sample shown in Fig. 2b the QD LO phonon feature is observed at ~254 cm^{-1} (Fig. 2b, spectrum 4). This indicates significant confinement causing the downward shift of the phonon line. The stronger phonon confinement effect in InAs QD's embedded in AlAs evidences their smaller average size compared to InAs QD's in a GaAs matrix. This is consistent with the results of *in situ* scanning tunneling microscopy studies of InAs/(Al,Ga)As self-assembled islands [13].

The phonon line of an InAs wetting layer (WL) is seen in the Raman spectra of InAs/AlAs QD's structures (Fig. 2b) at 244 cm^{-1}. This line was also observed in the Raman spectra of a planar superlattice $(AlAs)_{30}(InAs)_{1.5}$, having an InAs layer thickness just below the threshold of QD formation. This confirms its attribution to the WL phonons. This line has a lower frequency than the QD phonons because of the strong confinement in the thin wetting layer.

Figure 2c shows the Raman spectra of InAs/AlAs QD structures in the AlAs optical phonon region. Polarized spectra are dominated by two bands of interface phonons labeled IF1 and IF2. These bands are attributed to the interface phonons associated with two types of interfaces: the planar interface between WL and AlAs matrix and three-dimensional QD/matrix interface, respectively. Horizontal bars show the interface phonon bands calculated using the dielectric continuum model [14] for a planar superlattice and spherical clusters. The model provides reasonable agreement with experimental spectra. For the planar interface the calculated band is close to the AlAs LO phonon because of the high thickness ratio of AlAs and InAs layers. The experimentally observed IF1 band is slightly shifted to lower frequencies possibly due to the influence of strain, which is large near the planar interface. The relative contribution of the phonon band corresponding to WL/AlAs matrix interface (IF1) is larger for high excitation energies being closer to resonance with electronic transitions in the wetting layer.

Figure 3 illustrates the effect of growth temperature on the vibrational spectra of InAs QD's in AlAs matrix. The figure shows Raman spectra of a series of InAs QD's grown at substrate temperatures varied in the range of 420–520°C. As one can see, the LO phonon line of QD's grown at 420°C has the lowest frequency, i.e. the confinement is largest for this sample. This means that QD's grown at 420°C have the smallest average size. Increasing the growth temperature up to 480°C leads to the high-frequency shift of the InAs QD phonon line maximum and the decrease of its line width. This reveals the formation of larger InAs islands and

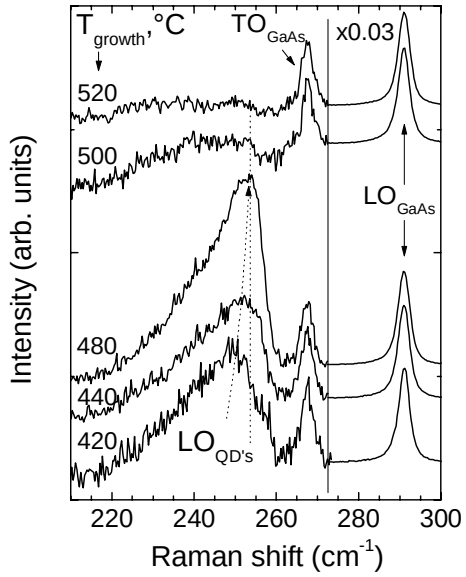

Figure 3. Raman spectra of InAs QD's in AlAs matrix, grown at different substrate temperatures. Dotted lines are guides to the eye.

improved size homogeneity. Further substrate temperature increase (500°C and higher) leads to the broadening of the QD phonon line, decrease of its frequency and intensity. This is most likely due to partial re-evaporation of InAs causing the decrease of QD size and density. In the sample grown at 550°C (not shown on Fig. 3) the evaporation of InAs leads to complete disappearance of the InAs phonon features in the Raman spectra.

We have performed the first experiments on synthesis of InAs QD's embedded in Al oxide. Preliminary Raman results show that depending on oxidation conditions (humidity, temperature) the InAs QD's in an aluminum oxide matrix can become fully relaxed [15] or even more highly strained than original InAs QD's in AlAs matrix before the oxidation. Figure 4 shows the micro-Raman spectra for an InAs QD sample after the AlAs oxidation. The spectrum taken from a non-oxidized area contains the LO and TO phonon peaks of AlAs layers, GaAs substrate, and the LO phonon line of InAs QD's. The spectra of an oxidized area show an increase of the InAs QD LO peak intensity and ~5 cm^{-1} shift of the phonon line position towards higher frequency. The first effect is explained by the wider bandgap of the aluminum oxide matrix compared to AlAs leading to a shift of confined electronic states in InAs QD's closer to resonance with the laser excitation energy. The high-frequency shift of the QD phonon line is caused by an increased mechanical strain in the InAs QD's due to shrinkage of the aluminum oxide layers in the oxidation process. At the boundaries of oxidized and non-oxidized areas two features appear in the Raman spectra, evidencing the presence of amorphous and crystalline As clusters. The crystalline As is characterized by the line at 198 cm^{-1}, while the broad band centered at 227 cm^{-1} corresponds to amorphous As [16]. It should be noted that we did not observe the characteristic lines of amorphous As_2O_3 at 475 cm^{-1}, indicating the absence of this possible product of the oxidation process. These first results demonstrate the formation of InAs QD's in wide bandgap matrix of aluminum oxide. However, optimization of the selective oxidation process is required to form InAs QD's with defined size and strain state as well as homogeneous oxide matrix.

SUMMARY

The phonon spectra of self-assembled InAs quantum dots in AlAs matrix were studied by Raman spectroscopy. The position, asymmetric lineshape of LO phonon lines of InAs QD's and the low-frequency shift with increasing excitation energy are explained by effects of strain, confinement and QD size distribution. Confined phonons of the InAs wetting layer are also

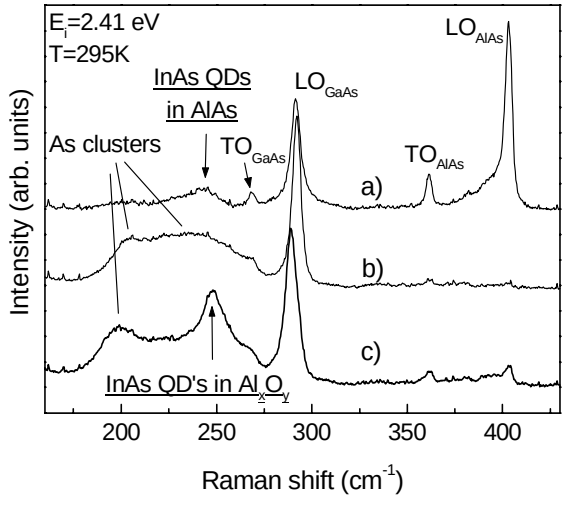

Figure 4. Raman spectra of InAs QD's after the oxidation of AlAs layers, taken from a non-oxidized area (a), a boundary of oxidized and non-oxidized areas (b), and an oxidized area (c).

observed in the Raman spectra. Two bands of interface phonons in the AlAs frequency region are attributed to phonons associated with two types of interfaces: the planar interface WL/AlAs matrix and the three-dimensional QD/matrix interface. Raman studies of a series of InAs QD's grown at different substrate temperatures demonstrated that increasing the growth temperature from 420 to 480°C leads to the formation of larger InAs QD's and improved size homogeneity. However, the temperature elevation up to 500°C and above causes partial re-evaporation of InAs leading to decrease of QD size and density, and, finally, their complete disappearance.

InAs QD's embedded in aluminum oxide were fabricated by selective oxidation of AlAs matrix of InAs/AlAs QD structures. Micro-Raman spectroscopy data allow determining the strain state in InAs QD's in an oxide matrix, which depends strongly on the oxidation conditions. Also, micro-Raman studies provide an evidence of the presence of such AlAs oxidation products as amorphous and crystalline As clusters at the boundary of oxidized/non-oxidized areas.

ACKNOWLEDGMENTS

The present study was supported by the Volkswagen Foundation (Project I/76 837) and the Russian Basic Research Foundation (Project 01-02-16969).

REFERENCES

1. D. Bimberg, M. Grundmann and N. N. Ledentsov, *Quantum Dot Heterostructures* (Wiley, New York, 1999)
2. D. Yoffe, Adv. Phys. **50** 1-208 (2001).
3. Polimeni, A. Patane, M. Henini, L. Eaves, and P. C. Main, Phys Rev B **59**, 5064 (1999).
4. Lee U H, Lee D, Lee H G, Noh S K, Leem J Y and Lee H J 1999 Appl Phys Lett 74 1597-99; Kim Y S, Lee U H, Lee D, Rhee S J, Leem Y A, Ko H S, Kim D H and Woo J C 2000 J Appl Phys 87 241-244
5. K. Pierz, Z. Ma, I. Hapke-Wurst, U. F. Keyser, U. Zeitler, and R. J. Haug, Physica E **13**, 761 (2002)
6. P. Dawson, Z. Ma, K. Pierz, and E. O. Göbel, Appl. Phys. Lett., **81**, 2349 (2001).
7. J. M. Dallesasse, N. Holonyak Jr., A. R. Sugg, T. A. Richard, and N. El-Zein, Appl Phys Lett **57**, 2844 (1990).
8. H. Richter, Z. P. Wang, and L. Ley, Solid State Commun. **39** (1981) 625.
9. I. H. Campbell and P. M. Fauchet, Solid State Commun. **58** (1986) 739.
10. M. Grundmann, O. Stier and D. Bimberg, Phys Rev B **52**, 11969 (1995).
11. R. Heitz, M. Veit, N. N. Ledentsov, A. Hoffmann, D. Bimberg, V. M. Ustinov, P. S. Kop'ev, and Zh. I. Alferov, Phys Rev B **56,** 10435 (1997)
12. Yu. A. Pusep, G. Zanelatto, S. W. Da Silva, J. C. Galzerani, P. P. Gonzalez-Borrero, A. I. Toropov, and P. Basmaji, Phys. Rev. B **58** R1770 (1998).
13. P. Ballet, J. B. Smathers, H. Yang, C. L. Workman, and G. J. Salamo, J. Appl. Phys. **90**, 481 (2001); P. Ballet, J. B. Smathers, and G. J. Salamo, Appl. Phys. Lett. **75**, 337 (1999).
14. P. A. Knipp and T. L. Reinecke, Phys. Rev. B **46**, 10310 (1992).
15. D. A. Tenne, O. R. Bajutova, A. K. Bakarov, A. K. Kalagin, A. G. Milekhin, A. I. Toropov, and D. R. T. Zahn, Tech. Phys. Lett **28**, 554 (2002).
16. C. I. H. Ashby, J. P. Sullivan, K. D. Choquette, K. M. Geib, and H. Q. Hou, J. Appl. Phys. **82**, 3134 (1997).